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OTS-modified HA and its toughening effect on PLLA/HA porous composite

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Abstract In this paper, hydroxyapatite (HA) particles was modified with long-chain organic silane-Octadecyltrichlorosilane (OTS), and the modified particles were further used for preparing Poly(L-lactic acid) PLLA/HA porous composite. The modified particles were characterized by means of XRD, FTIR, and XPS techniques. Both XPS and FTIR results showed that OTS had been combined with HA, and the formation of P–O–Si bond, a covalent bond, on the HA particle surface was confirmed by XPS. OTS-modified HA particles were used to prepare porous composites by thermally induced phase separation method. The results showed that the composite had an interconnected pore structure with 100–300 μm macropores. With OTS dosage increasing during modification, the mechanical properties of PLLA/OTS-modified HA porous composites increased obviously. These results showed that OTS modification can effectively improve the interface compatibility between HA surface and PLLA.

1 Introduction

Being similar to the major inorganic component of the hard tissue in human body, Synthetic Hydroxyapatite (HA) shows superior biocompatibility and osteoconductivity and finds many applications such as bone fillers [1, 2], coatings on orthopedic implants [3], fillers in inorganic/polymer composites [4] and one of the components of bone tissue engineering scaffolds [5–7].

The surface properties of HA play important roles in these applications. For example, in polymer/HA composites, in order to improve the interface between HA and polymer, HA should possesses hydrophobic surface, which can be done through surface-modification by organic molecules. Also, it is expected that such modification could provide not only significantly improved interface compatibility but also enhanced biological performances of HA particles.

There are two ways to modify the surface of HA by organic molecules. The first method is through surface adsorption [8]. It is known that many polymers and proteins can be physical adsorbed onto the surface of HA [9–12]. Physical adsorption means it may be easily be washed out in the physiological environment; Tanaka [13] found by TPD and FTIR that pyridine, *n*-butylamine, and acetic acid are adsorbed on HA by hydrogen-bonding to the surface P–OH groups of HA. The second approach is to graft organic molecules through covalent bonding to the hydroxyl groups which are available on the crystal surface of HA [8]. Covalent bonding to HA leading to a durable modified surface can protect modifier remaining from influence of blood and body fluid. Organic-silicone based modifier can covalently bond to surface hydroxyl groups through silanization reaction [14], thus silane coupling agents have been the focus of the research [15].

Many efforts have been made on silane coupling agents modified HA. Vaz [16] use silane coupling agents to enhance the interfacial interactions in starch—EVOH/hydroxylapatite composites. Santos [17] used organosilanes to control adhesion in polymer-HA composites and to

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improve the mechanical properties of dental materials. Labella [4] speculated that silane could be coupled to the surface of HA through the reaction with the surface hydroxyl groups of HA.

Among all the silane coupling agents, a long-chain organic silane, octadecyltrichlorosilane (OTS) is the best one to modify the surface of the HA. The reasons are as followings: first, Rao [18] pointed out in his studies, scanning force microscopy observations have confirmed that the fibrinogen molecule adsorbed to hydrophobicized surfaces retains its native structure. Tsortos [19] also pointed out that HSA and fibrinogen can be adsorbed to OTS-modified surface assumes a conformation that exposes nucleation sites for calcium phosphates. It means the biological performances of HA can be effectively and steadily improved by modifying it with OTS. Second, OTS has a longer hydrocarbon chains than short-chain silanes, which means a much more hydrophobic surface if it is successfully combined onto HA. That actually favors the interface compatibility between HA and polymers in composite materials.

In this work, OTS is used as coupling agent to modify the surface of HA by a silanization reaction, and the OTS-modified HA are characterized by means of XRD, FTIR and XPS techniques. PLLA/OTS-modified HA porous composites are further prepared and characterized for compressive strength, to evaluate the effect of surface-modification.

2 Materials and methods

2.1 Materials

HA powders were obtained from an amorphous Ca phosphate precursor way [20].The particles are around 30–50 nm in width and 80–120 nm in length. Octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$, OTS, Acros), 1,4-dioxane and Pluronic F127 (PF127), Toluene and PLLA with average molecular weight of 200,000 were used as obtained.

2.2 Methods

HA particles were first dried at 120°C for 24 h and added into OTS anhydrous toluene solution (2–6 mmol/l), after 20-min ultrasonically dispersing and 10-min rigorously stirring, designed amount of nano-sized HA powders were added into the solution and stirred for another 6 h at room temperature. Upon finishing, the particles were filtrated and washed for three times with the toluene solution to remove physically adsorbed OTS. Finally, the washed particles were dried in a vacuum oven at 120°C for 24 h to be OTS-modified HA particles.

In order to characterize the effect of such modification, porous modified-HA/PLLA scaffolds were prepared following a TIPS based method [21]: PLLA was dissolved in dioxane in the weight/volume percentage (w/v) of 5%, then PF127 (1.5% w/v) and 30 wt.% OTS-modified HA particles with different OTS content ($0 \sim 15$ wt.%) were added into the PLLA solution with stirring. The mixture was stirred at 80°C for 1 h to be homogeneous. Then, the mixture was directly put in a refrigerator maintained at −12°C for 12 h. Finally, the solvent was removed to obtain a porous composite by freeze-drying for 3–4 days in a freeze-dryer.

X-ray diffraction was employed to identify phases (XRD, RIGAKU, D-Max, RA, CuKα, 2°/min, 0.02 per step). The X-ray Photoelectron Spectroscopy (XPS) data were obtained using a X-ray Photoelectron Spectrometer (XPS, AXIS Kratos Ultra, Aluminum mono, 0.1 eV per step for narrow scan,), C1s peak at 284.6 eV was used for calibration. The Fourier Transform Infrared Spectroscopy (FTIR) were recorded using a Nicolet Avatar 360 spectrophotometer through a KBr pellet method.

The morphology of HA particles and OTS-modified HA particles was observed in a Transmission Electron Microscopy (TEM, JEOL 1200), The morphology of the PLLA/OTS-modified HA porous composites was observed in a Field Emission Scanning Electron Microscopy (FE-SEM, FEI SIRION).

Elastic modulus and compressive strength of the PLLA/OTS-modified HA porous composites were tested in a mechanical tester (Zwick Roell Z020, Germany), the crosshead speed was set at 1.0 mm/min.

3 Results and discussions

3.1 Crystalline phase of powders

In order to determine if there is any structural change during surface-modification, the unmodified HA and modified HA was characterized by XRD, and the results are given in Fig. 1. No remarkable change in XRD patterns was observed. The XRD patterns of the OTS-modified HA showed only the peaks due to HA and no pronounced change on crystallinity was recognized, This implies that the modification reaction has no effect on the crystal structure of the HA particles.

3.2 Morphology of the powders

Figure 2a, b are TEM micrographs of HA and OTS-modified HA particles, respectively. From Fig. 2, we can seen that the both HA particles and OTS-modified HA particles

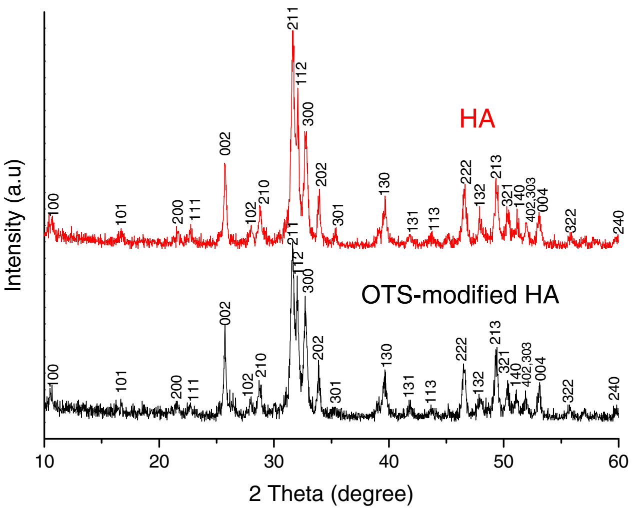


Fig. 1 XRD patterns of unmodified HA powder and OTS-modified HA powder (10 wt.% OTS)

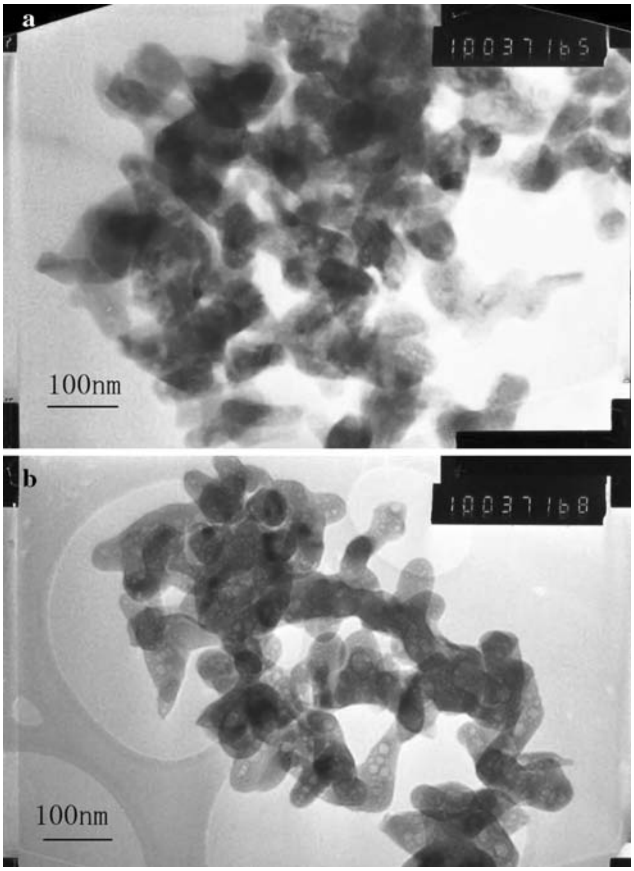


Fig. 2 TEM of HA particles: **a** pure HA particles, **b** OTS- modified HA particles (10 wt.% OTS)

all had (width:30–50 nm and length:80–120 nm) particle size, It means the surface-modification have not change particle size.

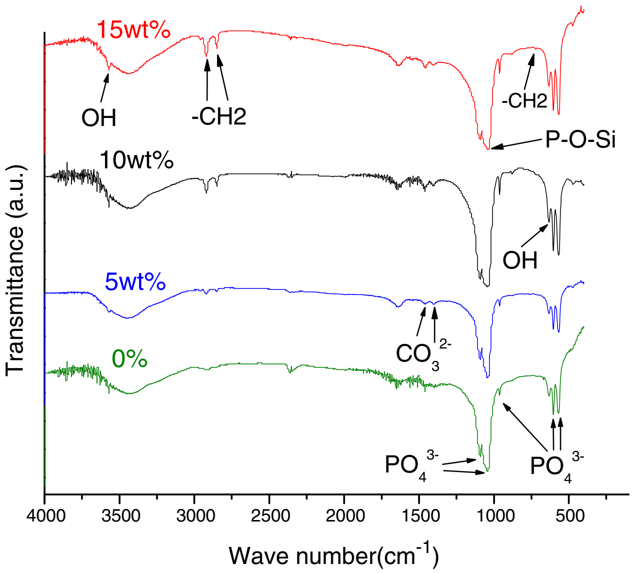


Fig. 3 FTIR spectra of unmodified HA and OTS-modified HA

3.3 Surface structure of powders

Figure 3 gives the FTIR spectra of unmodified HA and OTS-modified HA. Some of the main adsorption peaks were identified as follows: unmodified HA particles shows characteristic bands due to PO_4^{3-} groups (962, 1046, 1092, 566, and 606 cm^{-1}), OH^- groups in HA (3572 and 633 cm^{-1}) [22] and in adsorbed H_2O (1640 cm^{-1}) [23]. Bands at about 1403, 1457 and 873 cm^{-1} are ascribed to CO_3^{2-}, which is resulted from minor CO_3^{2-} inclusion in HA synthesis [22].

Besides these bands, OTS-modified HA exhibits C–H stretching bands at 2850 and 2920 cm^{-1}, and swaying mode at 725 cm^{-1} [23]. The intensity of these C–H related bands increases with increasing amount of OTS during modification reaction. It is noteworthy that one of the PO_4^{3-} stretching band shifts to low wavenumber direction significantly (from 1046 to 1030 cm^{-1}) after modification, the shift is attributed to the formation of P–O–Si bonding on the surface of silane modified HA [24–26]. That indicates the OTS molecules, at least partly, attach on HA surface through covalent bonds.

More detailed information is obtained through XPS, as shown in Fig. 4. In unmodified HA, the binding energy of P2p is 133.8 eV [27], which is attributed to PO_4^{3-}. After OTS modification, the P2p peak of OTS-modified HA can be deconvolved into two sub-peaks: 133.9 eV, which is from PO_4^{3-} in HA, and 133.2 eV, which is definitely from a different chemical state.

Since P2p binding energy shows a negative chemical shift, a chemical environment characterizing high electron density is formed. A possible explanation for this could be the P2p binding energy changes is contributed by that the

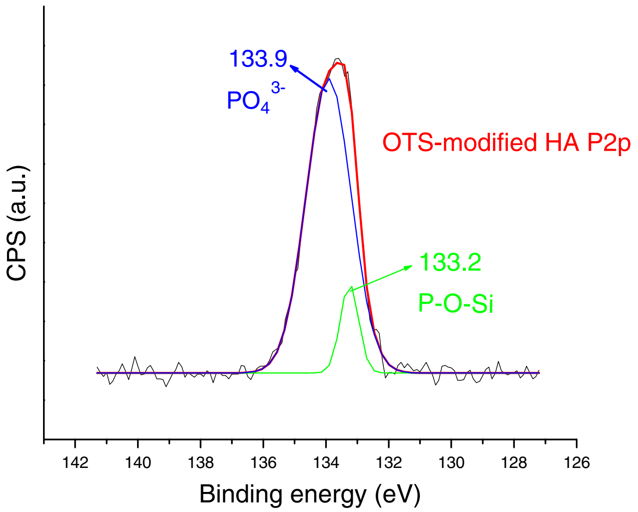


Fig. 4 XPS narrow spectra of P2p in OTS-modified HA (10 wt.% OTS)

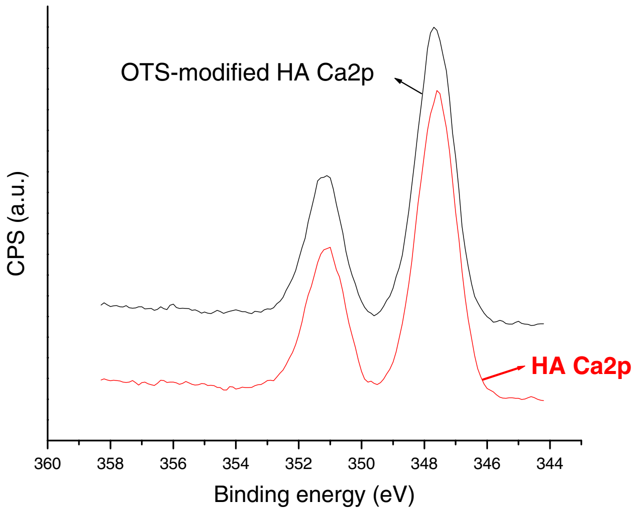


Fig. 5 XPS narrow spectra of Ca2p (10 wt.% OTS)

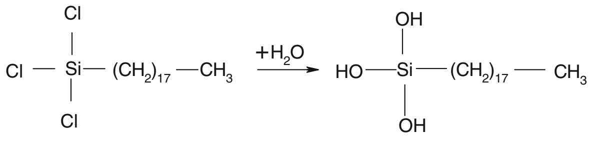
Table 1 Surface compositions of HA particles (at%)

OTS dosage	O	Ca	P	Si
0% (HA)	38.2	24.8	15.8	0
5 wt.%	27.4	19.2	13.8	2.0
10 wt.%	24.8	17.0	12.5	2.9
15 wt.%	22.2	15.2	10.6	2.7

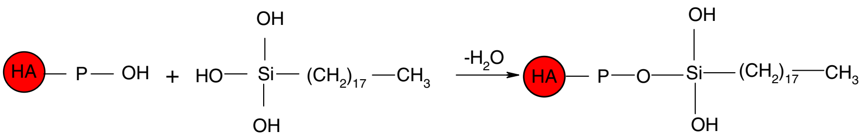
second-nearest neighbor groups, which plays important roles in determining the atoms binding energies [28], become less electronegative. This implies, H in –P–O–H is replaced by other element or radical whose electronegativity is lower than that of H.

The electronegativity of the elements in OTS is as following: H-2.20, C-2.45, Si-1.95, Cl-3.25. Only Si exhibits lower electronegativity than H. Based on such fact, it is reasonable to say H is replaced by Si. In other words, P–O–Si bond is formed in OTS-modified HA and OTS is covalently bonded onto the surface of HA.

As shown in Fig. 5, both unmodified HA and modified HA show the same Ca2p binding energy at 347.6 eV. That indicates the chemical state of Ca has no change before and after OTS modification. Such results further support that the OTS modification is actually through surface P–OH group. Most probably, the OTS modification is silanization process following a two step reaction: OTS first hydrolyzes into silanols (Eq. 1), and then reacts with the surface P–OH groups of HA (Eq. 2).



$$\mathrm{Cl}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{Si}}}-(\mathrm{CH_2})_{17}-\mathrm{CH_3} \xrightarrow{+\mathrm{H_2O}} \mathrm{HO}-\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{Si}}}-(\mathrm{CH_2})_{17}-\mathrm{CH_3} \qquad (1)$$



$$\text{HA}-\mathrm{P}-\mathrm{OH} + \mathrm{HO}-\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{Si}}}-(\mathrm{CH_2})_{17}-\mathrm{CH_3} \xrightarrow{-\mathrm{H_2O}} \text{HA}-\mathrm{P}-\mathrm{O}-\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{Si}}}-(\mathrm{CH_2})_{17}-\mathrm{CH_3} \qquad (2)$$

Ishikawa [29] found that HA surface has three kinds of P–OH groups acting as adsorption sites for CO_2, CH_3OH, CH_3I and H_2O. Tanaka [13] found by TPD and FTIR that pyridine, *n*-butylamine, and acetic acid are adsorbed on HA by hydrogen-bonding to the surface P–OH groups of HA. Both the FTIR and XPS results of our study further prove that in some cases, such as OTS modification, surface P–OH could even acts as an active chemical reaction site for covalent bonding.

The surface chemical compositions of HA and OTS-modified HA powders are calculated based on XPS detail scan results and tabulated in Table 1.

XPS analysis of HA surface elements showed that with increasing OTS addition amount, Si content first increases, and then saturates. That means the surface silanization extent could be regulated through varying OTS amount. However, such regulation becomes less effective when

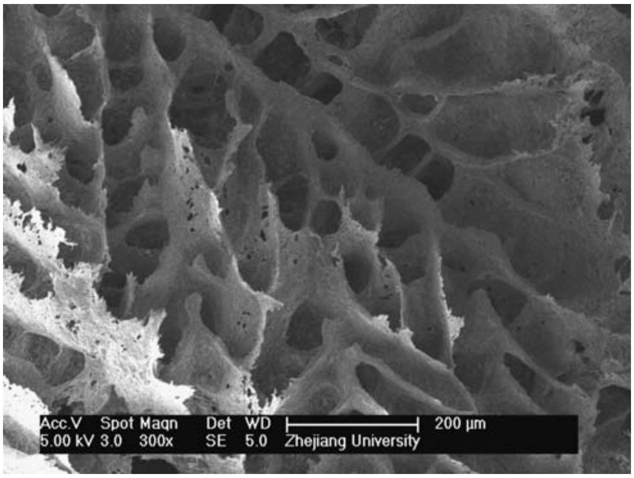


Fig. 6 Typical microstructure of the composite

OTS amount reaches 10 wt.%, since some OTS molecules begin to react with each other (self-condensation). As a result, the highest surface Si content in this work is about ~2.9 at%.

3.4 Mechanical properties of corresponding composite

Figure 6 gives the typical microstructure of corresponding PLLA/HA composites. All the samples showed similar microporous structure with 100–300 µm pores. To evaluate the effect of surface-modification of the HA-PLLA interface, as shown in Fig. 7, the compressive strength and elastic modulus are measured.

It can be seen from Fig. 7 that with increase of OTS content in HA particles, the mechanical properties of corresponding PLLA/OTS-modified HA porous composites improved obviously. For pure HA particles case, elastic modulus and compressive strength are 2.14 and 0.55 MPa, respectively; when OTS dosage reaches 15 wt.%, elastic modulus and compressive strength increases to 6.44 and 0.95 MPa, respectively. It showed that after HA surface-modification, elastic modulus becomes three times higher and compressive strength becomes two times higher.

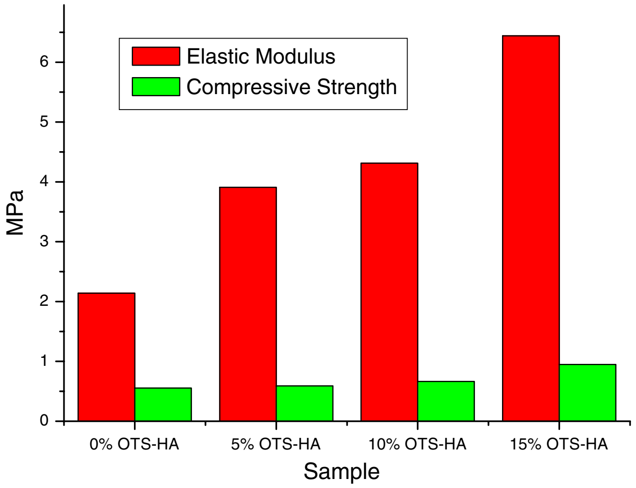


Fig. 7 Effect of OTS dosage on mechanical properties of PLLA/OTS-modified HA porous composites (HA contents are fixed at 30 wt.%)

The reasons for the improved mechanical properties of PLLA/OTS-modified HA porous composites are suggested as following: OTS has been covalently bonded on the surface of HA particles and increases the surface hydrophobicity, which improved the interface compatibility between OTS-modified HA surface and PLLA.

4 Conclusions

In this study, the Octadecyltrichlorosilane is successfully grafted onto the surface of hydroxyapatite through silanization reaction. XPS results shows that P–O–Si bond has been formed on HA surface and Si content can be adjusted in the range between 0 and 2.9 at%.

The mechanical properties of the PLLA/OTS-modified HA porous composites can be improved obviously. Comparing with unmodified HA, OTS-modified HA can lead to a composite with three times higher elastic modulus and two times higher compressive strength. The results also showed that OTS modification can effectively improve the interface compatibility between HA surface and PLLA.

These results imply OTS-modified HA is a good inorganic component in bone tissue engineering scaffolds and bone regenerative composite.

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